REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
05-02-2007	Technical Paper	

4. TITLE AND SUBTITLE

Role of Thermochemical Decomposition in Energetic Material Initiation Sensitivity and Explosive Performance (Preprint)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Scott A. Shackelford (AFRL/PRSP)

5d. PROJECT NUMBER
23030423

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRSP
10 E. Saturn Blvd.
Edwards AFB CA 93524-7680

8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-PR-ED-TP-2007-058

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-70448

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-PR-ED-TP-2007-058

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA# 07024A)

13. SUPPLEMENTARY NOTES
To be presented at the 10th International Seminar on "New Trends in Research of Energetic Materials," Pardubice, Czech Republic, 25-27 Apr 2007.

14. ABSTRACT

Catastrophic initiation of an energetic material consists of a complex, interactive, sequential train of mechanistic mechanical, physical, and chemical processes which occur over a finite time period and proceed from macroscopic into sub-microscopic composition levels (bulk > crystalline > molecular > atomic). Initiation results when these processes proceed at a rate which generates sufficient energy (heat) to reach a threshold stage within this finite time period. Thus, the rate at which these mechanistic processes occur defines initiation sensitivity and affects performance. Thermochemical decomposition processes regulate the rate at which heat energy is released at the molecular level, and therefore to some extent, control energetic material initiation sensitivity and performance characteristics. Kinetic deuterium isotope effect (KDIE) data, obtained during ambient pressure thermochemical decomposition process, identifies the mechanistic rate-controlling bond rupture which ultimately regulates the energy release rate of a given energetic material. This same rate-controlling bond rupture also appears as a significant rate-limiting feature in higher order deflagration, combustion, and explosion phenomena. The effect the KDIE-determined rate-controlling bond rupture exerts on initiation sensitivity, and its potential influence in combustion and explosion performance is delineated.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Dr. Scott Shackelford
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	31	**19b. TELEPHONE NUMBER** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**			N/A

Role of Thermochemical Decomposition in Energetic Material Initiation Sensitivity and Explosive Performance*) (Preprint)

Scott A. SHACKELFORD

Air Force Research Laboratory
10 East Saturn Blvd.
Edwards AFB, CA 93524-7680 (USA)
E-mail: scott.shackelford@edwards.af.mil

Abstract: Catastrophic initiation of an energetic material consists of a complex, interactive, sequential train of mechanistic mechanical, physical, and chemical processes which occur over a finite time period and proceed from macroscopic into sub-microscopic composition levels (bulk > crystalline > molecular > atomic). Initiation results when these processes proceed at a rate which generates sufficient energy (heat) to reach a threshold stage within this finite time period. Thus, the rate at which these mechanistic processes occur defines initiation sensitivity and affects performance. Thermochemical decomposition processes regulate the rate at which heat energy is released at the molecular level, and therefore to some extent, control energetic material initiation sensitivity and performance characteristics. Kinetic deuterium isotope effect (KDIE) data, obtained during the ambient pressure thermochemical decomposition process, identifies the mechanistic rate-controlling bond rupture which ultimately regulates the energy release rate of a given energetic material. This same rate-controlling bond rupture also appears as a significant rate-limiting feature in higher order deflagration, combustion, and explosion phenomena. The effect the KDIE-determined rate-controlling bond rupture exerts on initiation sensitivity, and its potential influence in combustion and explosion performance is delineated.

Keywords: energetic material, thermochemical decomposition, kinetic deuterium isotope effect, KDIE, initiation sensitivity, performance

Introduction

Initiation of an energetic material to a catastrophic event, like that reflected in deflagration, combustion, thermal explosion, and especially detonation phenomena, occurs when a mechanical

---

*) Presented at the 10th International Seminar "New Trends in Research of Energetic Materials", University of Pardubice, Pardubice, Czech Republic, April 25-27, 2007.

Distribution A. Approved for public release; distribution unlimited.

or thermal stimulus launches a sequential train of interactive mechanistic mechanical, physical, and chemical processes. These mechanistic processes proceed over a finite time period during which they sequentially pass from the macroscopic to sub-microscopic compositional levels (*i.e.* bulk, crystalline, molecular, atomic) [1]. Because of the many interactive processes involved with the energetic material initiation train sequence, and with the resultant sensitivity and performance characteristics, isolating any one process to elucidate its mechanistic contribution is quite difficult.

Use of the kinetic deuterium isotope effect (KDIE) approach to investigate ambient pressure thermochemical decomposition processes permits one to isolate and to determine the rate-controlling mechanistic feature which occurs at the molecular level [1, 2]. For a given energetic material, extension of the KDIE into higher order phenomena reveals that this same rate-controlling feature, observed during ambient pressure thermochemical decomposition, is mirrored in the rapid energy-releasing behavior of deflagration, combustion, thermal explosion, and detonation phenomena [3] which proceed through all or most composition levels [1]. Significant mechanistic clues to the relationship of thermochemical decomposition to energetic material initiation sensitivity and performance characteristics can be achieved using the KDIE approach.

Discussion

An overview of the mechanistic processes and their contribution to energetic material initiation and propagation to a catastrophic event provides a perspective for relating thermochemical decomposition to energetic material sensitivity and performance. A detailed review of KDIE investigations with ambient pressure thermochemical decomposition processes, and with higher order deflagration, combustion, and explosion phenomena, then reveals the mechanistic details of a relationship which rapid thermochemical decomposition has with sensitivity properties and performance characteristics. An updated general concept concerning energetic material sensitivity and initiation [1] provides the framework for this discussion.

General Concept Concerning Energetic Material Initiation and Sensitivity [1].

Depending upon the sensitivity properties of a given energetic material, a mechanical or thermal stimulus applied to it can result in the initiation of a catastrophic energy-releasing thermal event. Initiation of an energetic material into a catastrophic event, even with a

mechanical stimulus, is a heat-driven event [1, 4]. The initiation of an energetic material is viewed as a sequential train of interactive mechanistic mechanical, physical, and chemical processes which occur over a finite time period and which proceed from the macroscopic to sub-microscopic scale levels (bulk, crystalline, molecular, atomic). These mechanistic processes perform three necessary functions in the sequential initiation train [1].

The first mechanistic function is the formation of a physical environment and/or the use of an existing physical environment [4], where other subsequent mechanistic processes can occur. The second mechanistic function ensures the generation, transfer, and concentration of energy in the newly formed environment to generate heat and produce hot spots [1, 4]. A third mechanistic function initiates and promotes the rapid propagation and acceleration of the thermochemical decomposition process and its concomitant heat energy release to provide the chemical species and threshold energy needed to initiate and sustain combustion or drive an explosive shock wave to initiation.

Insert Figure 1

Over a finite time period, these three functions begin in the bulk material, proceed into lower compositional levels possibly continuing on through the atomic realm to produce final, mostly gaseous products which are detected back at the bulk level (Figure 1). Thus, the initiation sensitivity of a given energetic material is defined by the **rate** at which a given mechanical or thermal stimulus drives mechanistic processes to produce a **threshold energy** within an inherently defined **finite time period**. If all three interactive mechanistic functions proceed through all composition levels rapidly enough to produce heat and reach a sufficient energy threshold within this defined finite time period, initiation and propagation to a self-heating catastrophic event results. Conversely, when an interaction of mechanistic processes proceed at a rate too slowly within this time period to reach this heat-driven initiation threshold, no higher order catastrophic initiation and response result [1].

Therefore, decreasing the rate at which these mechanistic processes proceed should contribute to energetic material desensitization and/or decreased performance. Application of the KDIE to global thermochemical decomposition processes at the molecular level of this sequential initiation train identifies the rate-controlling mechanistic feature and demonstrates this feature to

be a noticeable factor in energetic material desensitization as well as in deflagration, combustion, and explosive performance characteristics [2, 3].

The update regarding a general concept for energetic material initiation and sensitivity [1], begins at the macroscopic compositional level and addresses the first mechanistic function. The first mechanistic function involves the formation of a physical environment, and/or the use of an existing physical environment, within which subsequent mechanistic processes can proceed. A sudden external mechanical stimulus (*e.g.* impact, shock, friction) on a solid energetic material (Figure 1 @ A) results in various physical responses (*e.g.* fracture, shear band formation, visual localized ignition, plastic deformation, viscous flow, adiabatic gas bubble compression, and others) at the bulk scale (Figure 1 @ B). Some of these material alterations can be visually observed at the bulk compositional scale [4], while others require high resolution atomic force microscopy (ATM) to be studied [6]. These actual physical responses and their degree of importance varies with the type of mechanical stimulus encountered as well as with energetic material properties determined by inherent crystal habit and chemical structure [1]. ATM investigation reveals the formation of shear band disruptions in the energetic material [6]. Formation of these shear bands disrupts the crystal morphology and begins producing heat energy (Figure 1 @ B). The net result of mechanical stimulus at the bulk level is the formation of additional microstructural inhomogeneities or defects, at the crystalline level, in addition to those already present in the crystal lattice (Figure 1 @ C). These defects then can serve as highly localized nucleation points for the generation, transfer, and concentration of energy. Thus, the first mechanistic function is fulfilled; mechanical stimuli form a physical environment where subsequent physicochemical and thermochemical mechanistic processes can proceed.

The second mechanistic function involves physicochemical processes which occur at the crystalline or microstructural level to generate, transfer, and concentrate heat energy at both the newly formed and inherently existing crystalline defects. Noted along the ATM observed shear bands from shock and impact are chains of extruded molten material beads as well as small dislocation cavities. The extruded molten beads mirror the presence of physicochemical mechanisms that generate heat and lead to hot spot formation. It appears that plastic flow during shear band formation deforms and distorts crystal lattice structure, and possibly molecular structure [6]. Also noted along these shear bands are small dislocation cavities. This crystal lattice deformation, resulting from shear band development, occurs from the formation and

movement of dislocations in the crystal lattice [6, 7]. The friction created along sliding crystal lattice interfaces [4], as the bulk material is disrupted, forms additional microstructural inhomogeneities or defects while releasing heat energy. An extreme acceleration in defect formation comes from a dislocation pile-up avalanche mechanism [8] resulting in numerous new crystalline level defects.

The mechanical energy which disrupts and deforms the crystal lattice along the shear bands is transformed into heat energy as the energy binding a well-ordered crystalline lattice is disrupted and released at these localized sites as heat energy (Figure 1 @ C). A recent experimental correlation between impact sensitivity and the heat of fusion lends additional support to this interpretation [9]. This deformation-generated heat is transferred and concentrated at these new defect sites where a large surface area exists. This rapid heat generation produces the myriad of hot spots as reflected by the molten beads and small dislocation cavities seen by the ATM shear band analyses. Adiabatic compression of trapped gas spaces in voids inherent with the bulk material [10] is another facet which also concomitantly generates heat and contributes to hot spot formation [6]. ATM investigation also reveals that thermal stimulus can promote defect formation, from uneven crystal expansion [7], where a similar energy concentration, like that produced for the mechanical stimuli, could result. Completion of the second mechanistic function to generate, transfer, and concentrate heat energy (Figure 1 @ B) and form defect hot spots (Figure 1 @ C) leads into the third mechanistic function.

The third mechanistic function occurs at the molecular and atomic levels within the newly formed hot spots. This function involves mechanistic processes that start and propagate kinetically controlled chemical reactions (Figure 1 @ D) which drive rapidly accelerating thermochemical decomposition and energy release to the initiation threshold. Both condensed phase (Figure 1 @ E) and subsequent gas phase (Figure 1 @ F) thermochemical decomposition processes are present in the sequential initiation train. The condensed phase thermochemical decomposition process begins by two methods.

The first method deals with the generation of non-thermally or physically (versus chemically) generated reactive radical species [11]. Along with the heat energy from crystal lattice deformation, these non-thermal radicals form, at the molecular level, during crystal deformation and dislocation at the crystalline level along crystal shear bands and on the resultant large surface area of the defects produced [8]. Highly reactive radical species are needed to start

the chemical reactions which drive thermochemical decomposition processes (Figure 1 @ D). Mechanically forced (shock, impact, and possibly friction) crystal dislocations during shear band formation, and resultant crystal lattice surface shifts, cause molecules in the crystal lattice to deform and move past one another. This movement of molecules can cause physical bond rupture (homolysis) when molecules encounter sufficient steric hindrance to collide into one another or to come into very close contact at distances longer than a normal bond distance but shorter than a Van der Waals radii [12]. This mechanistic non-thermal radical formation process is verified by computational [13, 14] and experimental diamond anvil [15] studies with nitromethane which show that certain crystal orientations of energetic molecules can be initiated to explosion more readily than others. Molecules which can slide by one another unimpeded in more favorable crystalline orientations are less sensitive to initiation. The experimental dependence of RDX detonation velocity with various crystal structure orientations [16] conceivably also reflects the ease with which non-thermal radicals are generated to start and initially help propagate the chemical reactions that produce the rapid condensed phase thermochemical decomposition process.

The second method that starts and accelerates the condensed phase thermochemical decomposition involves the localized heat energy that is concentrated on the inner high surface areas of the hot spot (Figure 1 @ E). These high temperatures increase the vibrational energy above ground state level in the chemical bonds of the energetic material molecules to the point that the weakest bond or trigger linkage, also termed first reaction [17], ruptures to form very reactive radical species. These chemically-generated thermal radical species also initiate, propagate, and then accelerate the reactions driving the thermochemical decomposition process. Electronic excitation has been suggested as one contributing mechanistic step in a multiprocess detonation model [18], and such electronic molecular excitation has been experimentally related to explosive shock and impact stimuli using X-ray photoelectron analysis [19] and first reaction studies [20]. Both mechanistic radical generating processes, non-thermal (Figure 1 @ D) and thermal (Figure 1 @ E), can generate reactive radical species that catalytically start, accelerate, and propagate the chemical reactions needed to drive thermochemical decomposition.

The start of the thermochemical decomposition process introduces kinetic control into energetic material sensitivity and the initiation concept. Thermochemical decomposition processes in solid energetic materials begin and accelerate in the condensed phase (Figure 1 @

E) and move into the gas phase (Figure 1 @ F).

Condensed phase thermochemical decomposition predominantly involves complex bimolecular [21], and to some degree intramolecular, chemical reactions to produce condensed phase intermediate compounds which decompose further into gaseous products with an additional concomitant heat energy release. KDIE experiments validate that the kinetic control in the condensed phase significantly determine the rate at which the overall global thermochemical decomposition process propagates and accelerates [1, 2, 22, 23]. This mechanistic process, ultimately, is controlled in the condensed phase [3, 24] since gas phase reactions proceed faster.

At the molecular level, formation of gas phase products from the condensed phase thermochemical decomposition process results in development of a propagating shock wave with cell-like structural features at the macroscopic level (Figure 1 @ F). It is behind this propagating wave that decomposing energetic molecules and their resultant energy release rates drive the shock front progressing through the initiating energetic material [1]. As demonstrated with shock tube experimentation, this cellular wave structure can define critical diameter since detonation occurs whenever the critical diameter is greater than 13 times the wave cell size [25]. Wave cell size is affected by the gas phase reaction kinetics, and the resultant energy release rate [26] from these decomposing gaseous products. Furthermore, this gaseous energy release rate can be altered by catalytic or inhibitor species, and a faster gaseous decomposition rate increases the sensitivity to detonation initiation [27].

At this point, energetic material initiation moves into the atomic scale of decomposed matter (Figure 1 @ G). The gaseous products following the shock wave, and derived from the molecular level condensed phase thermochemical decomposition process, break down further until atomization apparently occurs. This transition into the atomic compositional level (Figure 1 @ G) would mean that all chemical bonds rupture to form atomic species which now drive the shock wave before re-combining into final detonation products (Figure 1 @ H) [28].

The degree that this atomization occurs depends on the type of energetic material. With a homogeneous ideal explosive, which delivers the amount of energy expected, all bonds in the gaseous decomposition products eventually rupture creating a sustained atomic level equilibrium where complete randomization occurs with the interacting atoms. This is shown with $^{13}C/^{18}O$ isotopically labeled carbonyl groups in the homogenous explosive, *bis*-[2,2,2-trinitroethyl]

adipate, where complete random atom scrambling is observed in its detonation products [CO_2, CO, CH_4, O_2, C(s)] [28]. The same conditions applied to a non-ideal explosive formulation, Amatol 80/20, showed only a 12% mixing of ^{15}N nitrogen atoms with normal ^{14}N atoms in its nitrogen (N_2) detonation product ($^{15}N^{15}N$, $^{15}N^{14}N$, and $^{14}N^{14}N$) from labeled ammonium nitrate (20%), $^{15}NH_4{}^{15}NO_3$, and unlabeled TNT (80%) with its pendant $^{14}NO_2$ nitro groups. This low degree of isotopic scrambling is attributed to diffusion control of atomic species behind the detonation wave front [28], although slower reaction kinetics may also play a role since not all energy is released from a non-ideal explosive formulation [1]. Such a study has not been applied to either deflagration or high pressure combustion products. At this point, the third mechanistic function that addresses the start, propagation, and acceleration of the chemical reaction, which drive the thermochemical decomposition process to produce the molecular and atomic species, is complete. This results in high energy chemical species which drive the shock wave through an energetic material and finally culminate in the production of the chemical products measured at the bulk scale (Figure 1 @ H).

At least three compositional levels or scales, and in some cases four, are involved in the initiation and energy release of an energetic material undergoing a catastrophic event represented by deflagration, combustion, thermal explosion, or especially, detonation phenomena. Each has its own unique mechanistic processes which all interact over a finite time period within which a threshold of energy must be generated to achieve initiation from a sustained energy release. At each level, there are rate-controlling mechanistic features which can affect whether or not this threshold energy is reached in the finite time required. More sensitive energetic materials reach this initiation and sustaining energy threshold more easily (rapidly) than others. Here, rate-controlling mechanistic processes proceed at a faster rate. A less sensitive energetic material, under identically stressed conditions, will reflect rate-controlling mechanistic features that occur at a slower rate, where the rate is slow enough that initiation will not occur or where the sustained energy releasing process is slowed enough that performance is reduced. The rate at which mechanistic processes proceed affects energetic material sensitivity and performance. This is verified at the molecular level by KDIE-based mechanistic studies of the global thermochemical decomposition process and their comparison with higher order phenomena [1-3].

Distribution A. Approved for public release; distribution unlimited.

KDIE and Energetic Material Thermochemical Decomposition Processes.

At the molecular composition level, application of the KDIE to neat (non-solvent) condensed phase chemical reactions proceeding during the global condensed phase thermochemical decomposition process establishes a relationship between mechanistic rate and both energetic material initiation sensitivity and performance properties. The thermochemical decomposition begins in the many hot spots formed during the initiation train, but then rapidly spreads into the entire energetic material.

Condensed phase neat thermochemical decomposition processes consist primarily of a complex mechanistic set of bimolecular reactions with some degree of intramolecular character where two key homolytic bond ruptures occur. First is the **initial bond rupture**, also termed trigger linkage or first reaction [20], which determines the specific pathway the thermochemical decomposition process will follow and controls the decomposition products which will form [22]. Certain structural groups in an energetic molecule are centers for this initial bond rupture site (explosophores) [17]. Common explosophores and their initial bond rupture (-), contained in more familiar energetic materials, are C-NO_2, N-O in the nitro (NO_2) group, N-NO_2, O-NO, and C-NO. Once this pathway is established, many subsequent chemical reaction channels proceed which occur in series and competing parallel sequences. Along this decomposition pathway, one chemical reaction in a specific reaction channel proceeds significantly more slowly than all others. It is during this slowest reaction where the second key mechanistic bond rupture occurs, the **rate-controlling bond rupture**, which regulates the overall rate at which the global thermochemical decomposition process proceeds. This KDIE-determined rate-controlling bond rupture, accompanied by a concomitant atom transfer [29], usually occurs early in the condensed phase decomposition process [2, 22, 23, 30].

Insert Figure 2

As seen later, this kinetically governed rate-controlling bond rupture can have a significant effect on the overall energetic material initiation train sensitivity and on higher order performance. To date, this rate-controlling bond rupture cannot be identified by computational methods and must be determined experimentally using the KDIE approach.

The KDIE approach exploits the ground state vibrational energy difference of 2.3 kcal/mol

(9.6 kJ/mol) between the hydrogen atom bonded to a carbon atom and its deuterium isotope bonded to the same carbon atom of a specific molecule. Because of its higher mass, the bonded deuterium atom resides in a much lower 2.3 kcal/mol (9.6 kJ.mol) vibrational energy state. With an energetic material like TNT, a deuterium labeled C-D bond is stronger and more difficult to rupture during a chemical reaction than its analogous C-H bond in normal TNT. Therefore under identical thermochemical decomposition conditions, the C-D will rupture more slowly than the C-H bond because more energy over a longer time period must be transferred into the C-D bond vibrational ground state to achieve a homolytic bond rupture. However, this difference is detected in the global reaction kinetics of a thermochemical decomposition process only when the C-H and C-D bond ruptures occur during the slowest reaction step of the major, probably longest, and highest contributing channel of the many reaction channels in the decomposition pathway. Comparison of the different global reaction rates between C-H and C-D bond rupture affords a primary KDIE value when a ratio of their rates is equal to or greater than 1.41 theoretically and is as low as 1.35 experimentally [29]. If the rate-controlling step involves a bond rupture either a distance of one or two bonds removed from the deuterium labeled atom, a secondary KDIE is seen with a ratio value greater than 1.00 but less than 1.34 [29]. Both types constitute a positive KDIE response.

A primary KDIE usually defines this rate-controlling mechanistic step for the global thermochemical decomposition process, and normally is expressed as a ratio of the reaction rate constants (k_h/k_d) derived from the normal energetic material and its deuterium labeled analogue. KDIE values also have also been determined using induction period times (t_i) which are inversely proportional (t_{id}/t_{ih}) to rate constants [2, 22, 23, 29, 30]. Interestingly, the same KDIE determined rate-controlling step found for the ambient pressure condensed phase thermochemical decomposition process of a given energetic material is mirrored as a significant rate-controlling feature in higher order deflagration, combustion, and explosion phenomena [2, 5]. This is shown by KDIE behavior which has been detected in combustion burn rates [24,31], critical temperature measurements [32] as well as in impact, and shock initiation responses [33, 34].

The first application of the KDIE to a thermochemical decomposition, and its global reaction kinetics, occurred with neat molten TNT and its methyl deuterium labeled TNT-α-d_3 analogue using isothermal DSC analysis [30]. Here, early in the thermochemical decomposition process,

C-H bond rupture proved to be the rate-controlling step (Figure 2) and was especially predominant during the endothermic induction period (KDIE = 1.66). About 16 years later, it was suggested that induction period oxidation reactions at the pendant TNT methyl ($-CH_3$) group dominate in this portion of the thermochemical decomposition process [35] where these oxidation reactions all structurally must involve C-H bond rupture [2, 30]. The formation of 2,4-dinitroanthanil also cannot be ruled out from forming during the induction period because it catalyzes and accelerates the TNT thermochemical decomposition rate [36], as can the oxidation product 2,4,6-trinitobenzaldehyde [35], and other free radical sources (Figure 3) [35, 37]. Further support of this free radical catalysis and acceleration of induction period results from the fact that the free radical precursor, hydroquinone, greatly accelerates the TNT induction period as does benzoic acid to a small extent [30]. During the induction period, a threshold amount of catalytic material forms from the TNT itself, then starts, accelerates, and sustains the remainder of the TNT exothermic decomposition process [30]. The exothermic portion of the decomposition consisted of an acceleratory and subsequent decay phase. The decay phase KDIE is diluted to a lower 1.35 value because intermediate decomposition products react further to form later condensed phase products which do not involve C-H bond rupture as a rate-controlling step [30]. An independently conducted isothermal DSC thermochemical decomposition study of TNT reveals greater than 90% of TNT can be decomposed prior to entering the decay phase [2, 38].

Insert Figure 3

Subsequently, KDIE-based rate-controlling bond rupture was determined for the thermochemical decomposition processes using isothermal DSC, TGA, and reaction quenching UV methods with solid state TATB [32], solid, mixed melt, and liquid state HMX [29, 34, 40], solid and liquid state RDX [34, 39, 41], as well as solid and liquid state DNNC [22, 23], (1,3,5,5-tetranitrohexahydropyrimidine)**.** Figure 2 illustrates the KDIE determined rate-controlling bond ruptures which regulate the thermochemical decomposition process and its resultant energy release rate for several energetic materials.

In summary, liquid state TNT [30], solid state HMX [29, 34], both liquid and solid state RDX [34, 39, 41], and liquid state DNNC [23] show C-H bond rupture to be the rate-controlling step. The rate-controlling step for HMX and DNNC display a dependence on physical state.

Liquid state HMX [29] and solid state DNNC [22], during its endothermic induction period, display a secondary KDIE. A secondary KDIE indicates that ring C-N bond rupture likely is the rate controlling step under these decomposition conditions. HMX in its mixed melt state [29] displays an inverse KDIE suggesting that the rate at which its crystal lattice energy is overcome to convert from the solid to liquid state is the rate-controlling feature [29]. Solid state DNNC [22], once through its endothermic induction period where a catalytic species likely forms via C-N ring bond rupture, displays C-H bond rupture as its rate-controlling step during the exothermic accelerating energy-releasing phase of its thermochemical decomposition. Solid state TATB [32] decomposition shows N-H bond rupture to be its rate-controlling step.

The presence of hot spots, and the rapid thermochemical decomposition process occurring therein, is verified by scanning electron microscopy (SEM) and X-ray photoelectron spectra (XPS) investigations of energetic materials which were impacted or shocked just below their explosive initiation threshold. Micron-sized (impact) and submicron-sized (shock) defects with quenched, charred inner surfaces (hot spots) are seen via SEM analysis. Subsequent XPS studies of the charred inner defect surface identifies condensed phase decomposition reaction products for TATB [42], RDX [43]**,** and TNT [44] which mirror those also seen in ambient pressure thermochemical decomposition product analyses for TATB [45] and TNT [46, 47]. Additionally, a recent investigation of shock initiated TNT, followed by LC-UV analysis of its resultant solid residue products, further supports these sub-initiation approach results by detecting surviving condensed phase products which are the same as those found in ambient pressure thermochemical decomposition products (Figure 3) [48]. Especially notable is that these condensed phase decomposition products, detected from the sub-initiation impact and shock condensed phase products for TNT, TATB, and RDX, could only form by traversing through the KDIE-determined rate-controlling bond rupture found during ambient pressure thermochemical decomposition (Figure 3) [3]. The one exception is the nitroso products known to form from sub-initiated shock and drop-weight impacted RDX [43]. These reported products involve only one type of bond rupture (N-O) at the explosophore position as the nitro group is converted to a nitroso group. This N-O bond homolysis reflects the initial bond rupture (first reaction); the rate-controlling C-H bond rupture must occur later. The drop weight impacted sub-initiated RDX sample gives only decomposed nitroso products [43b]; however, the more extremely shocked sub-initiation RDX sample yields both the nitroso compound amd melamine types of structural

features where C-H bond rupture does occur [43a].

Thus, through use of the KDIE approach at the molecular composition level, the significance and actual role that the rapid thermochemical decomposition process plays in the energetic material initiation process is verified and established. Furthermore, the KDIE itself is validated as a potent method for determining specific rate-controlling features and critical mechanistic relationships in highly complex and extreme chemical environments.

Insert Figure 4

Relationship of Thermochemical Decomposition to Energetic Material Sensitivity and Performance.

KDIE mechanistic investigations show a distinct relationship between kinetically governed reaction rates and the rate-controlling steps found in thermochemical decomposition processes with both energetic material sensitivity and performance characteristics. This is reflected in KDIE investigations where deuterium labeled energetic materials alter combustion burn rates [24, 31], initiation thresholds [32-34], and detonation velocity [33].

Sensitivity. Explosive experiments conducted with a number of energetic materials and their deuterium labeled analogues reveal that, with one exception [3], the deuterium labeled compounds are more difficult to initiate. These energetic materials display a primary KDIE in their condensed phase thermochemical decomposition where C-H bond rupture (HMX, RDX, TNT), or N-H bond rupture (TATB) is the rate-controlling step [3]. Desensitization appears because deuterium atom substitution decreases the rate-controlling bond rupture and slows the thermochemical decomposition process regulating the energy release or generation rate. As suggested by the general concept concerning energetic material sensitivity and initiation [1], slowing the chemical kinetics and the resultant overall thermochemical decomposition process causes an insufficient energy generation rate during the required finite time period needed to reach the rate dependent energy threshold required for explosive initiation; and therefore, energetic material sensitivity is affected [1]. Thus, desensitization can be achieved by increasing the energy needed to effect a homolytic rate-controlling covalent bond rupture in the global thermochemical decomposition process, which in turn, decreases its resultant energy release rate below that needed to reach the explosive initiation threshold. The stated one exception above

deals with a Henkin test-based critical temperature measurement of HMX and HMX-d_8. Here HMX-d_8 displays a lower critical temperature for thermal explosion initiation (faster rate) and reflects an inverse KDIE behavior [3] previously exhibited during its mixed melt acceleratory portion of the ambient pressure thermochemical decomposition process (Figure 2) [2,29]. This behavior suggests solid state HMX-d_8 converts more rapidly than HMX into its mixed melt phase during the high confinement required for Henkin test samples and is initiated from the mixed melt phase before sample liquefaction occurs [3].

Critical temperature determination using the Henkin test with TATB and its TATB-d_6 analogue provides critical temperatures of 354 ^{o}C and 366 ^{o}C, respectively [32]. The 12 ^{o}C lower temperature for unlabeled TATB reflects a faster rate for the thermochemical decomposition process at 354 ^{o}C during this isothermal heat-initiated thermal explosion. It reflects a definite positive KDIE response when comparing TATB and TATB-d_6. This suggests that pendant amino group N-H bond rupture, seen in solid state TATB/TATB-d_6 ambient pressure thermochemical decomposition process (KDIE = 1.5), is the rate-controlling step for this TATB thermal explosion initiation [3, 32]. Deuterium labeled TATB-d_6 requires additional energy for the chemical reactions driving its thermochemical decomposition process to achieve the same decomposition rate as those for unlabeled TATB. In order to initiate a thermal explosion with TATB-d_6, additional energy must be provided by raising the temperature to 366 ^{o}C to achieve a rate-controlling step (N-D bond rupture) which, during the global thermochemical decomposition process, proceeds as fast as that of TATB at its lower 354 ^{o}C critical temperature. Thus, the decreased speed of the TATB-d_6 kinetically governed rate-controlling step (N-D bond rupture) slows the overall thermochemical decomposition process and reduces the amount of energy which it delivers within a necessary finite time period. This decreased TATB-d_6 energy release rate fails to provide the energy sufficient to reach the required explosive initiation threshold at 354 ^{o}C and results in a desensitized energetic material. In this same study, DINGU also displayed a higher critical temperature with its deuterium labeled analogue [32].

Shock induced detonation with HMX and RDX [34], as well as TNT [33]**,** and their deuterium labeled analogues, display a degree of desensitization. This is revealed by use of the KDIE approach in conjunction with the exploding metal foil method. In all three cases, the deuterium labeled analogues require a stronger shock from an explosion driven flyer plate

(higher plate velocity) to initiate detonation as shown: HMX vs. HMX-d_8 = 2.27 vs. 2.37 mm/μsec; RDX vs. RDX-d_6 = 2.33 vs. 2.41 mm/μsec; and, TNT vs. TNT-α-d_3 = 3.309 vs. 3.681 mm/μsec. While a ratio of the flyer plate velocities, used to initiate the detonation response, give a value smaller than what is seen in the primary KDIE values for their corresponding thermochemical decomposition processes (Figure 2), the differences in flyer plate velocities are statistically significant.

Because shock detonation initiation involves all the mechanistic processes at all compositional levels of matter, and is not solely limited to the molecular level thermochemical decomposition process, flyer plate shock magnitude differences in mm/μsec, as shown with TNT and TNT-α-d_3 (KDIE = 3.681 / 3.309 = 1.11) [33], are not the same as those seen for the corresponding global thermochemical decomposition rates during the induction period (KDIE = 1.66) [30]. Even though the induction period portion of the TNT thermochemical decomposition may be involved with the shock initiated detonation event [35], one should not expect the same KDIE value for shock initiation and thermochemical decomposition where C-H bond rupture controls the rate-controlling step. If one could isolate and individually measure the other mechanistic processes occurring during the entire shock initiated detonation event, many likely would show no difference between TNT and TNT-α-d_3 and contribute a percentage of this same response (*i.e.* a KDIE = 1.00) to the entire initiation event for both the normal and deuterium labeled energetic materials. For example, the magnitude of the TNT/TNT-α-d_3 induction period KDIE, from [KDIE = 493 sec (TNT-α-d_3) divided by 297 sec (TNT) = 1.66], can be diluted or reduced when measured in the presence of other contributing processes as shown: (*generic example only*); 493 s (TNT-α-d_3) + 500 s (other process) divided by 297 s (TNT) + 500 s (same other process) = 1.25]. All mechanistic processes contribute to the flyer plate velocity values during shock initiation; therefore, differences between the normal and deuterium labeled energetic material during the initiation event will be much smaller that what is derived from an isolated KDIE investigation of an isolated thermochemical decomposition process.

KDIE dilution by competing or interfering processes is a recognized concept and documented reality. It has been suggested that pendant methyl (-CH_3) group rate-controlling C-H bond rupture in the TNT induction period, of the thermochemical decomposition, occurs during higher order shock and mechanical impact initiation, and that it competes with a C-NO_2 bond rupture [35]. If this situation exists, a diluted KDIE value from that determined solely from an ambient

pressure thermochemical decomposition would result [35]. This cited dilution would be caused by competing chemical reaction channels at the molecular level. A documented TNT/ TNT-α-d_3 KDIE dilution does occur when thermochemical decomposition rate measurements are taken from the decay phase portion of the entire ambient pressure decomposition process [30]. In this case, a significant degree of intermediate condensed phase products, produced during the later stages of the TNT decomposition, react further without undergoing a rate-controlling C-H bond rupture and contribute no KDIE difference (KDIE = 1.00) between TNT and TNT-α-d_3. Thus, the KDIE obtained in the late decay portion of the TNT decomposition process (KDIE = 1.35) is diluted from that found early during the induction period when the initial catalytic product(s) (possibly 2,4-dinitroanthranil or methyl group oxidized compounds) form via a rate-controlling C-H bond rupture (KDIE = 1.66) [30]. It has been shown that greater than 90% of TNT can decompose before the thermochemical decomposition process reaches the decay phase portion [38]. Even if only the induction period portion of the thermochemical decomposition process is involved in shock or impact initiation, this latter KDIE dilution likely still would be seen because of the other non-differentiating KDIE processes proceeding at other compositional levels.

Because the only difference in normal HMX, RDX, and TNT, and their corresponding deuterium labeled compounds, comes from deuterium isotope substitution, rate-controlling C-H bond rupture, seen in thermochemical decomposition, is suggested to be a significant regulating mechanistic feature for shock detonation initiation of these explosives. The differences in the flyer plate velocity shock initiation reveal that the rate-controlling step (C-H bond rupture), present during the thermochemical decomposition process of HMX, RDX, and TNT, also is present during their initiation train sequence to detonation. Additional verification of this fact comes from the XPS detection of decomposition products on the charred inner surface of hot spots formed from sub-initiation experiments with RDX and TNT [43, 44]. In the charred hot spot surface, the decomposed products formed must involve the same C-H bond rupture as that found for the rate-controlling step of the thermochemical decomposition process [30, 34, 39]. Furthermore, the same products in shock initiated TNT residue, as those which are produced from the ambient pressure thermochemical decomposition process [46, 47], have been reported [48], and no condensed products were found that could be attributed to being formed from an alternative C-NO_2 bond rupture. Only those products which must involve the rate-controlling C-H bond rupture for the TNT thermochemical decomposition process [30] were identified [48].

This could mean a competing C-NO_2 bond rupture is not highly prevalent in TNT shock initiation, or that resultant intermediate condensed phase products produced from this C-NO_2 homolysis reaction channel, are unstable enough that they continue reacting to form only gas phase products. Finally, high pressure diamond anvil studies of nitromethane (CH_3NO_2) decomposition at 7 GPa pressure, not only shows it to be more sensitive to explosive initiation in certain crystalline orientations, but also reveals that deuterium-labeled nitromethane-d_3 (CD_3NO_2) fails to explode under any similar condition [15]. This behavior further illustrates how energetic material sensitivity can be altered and decreased by slowing the kinetically governed rate-controlling step, and resultant thermochemical decomposition energy release rate by deuterium substitution.

Clearly, an energetic material is desensitized by deuterium labeling which can cause a KDIE response. As shown by the shock induced detonation response of TNT, HMX, and RDX, thermochemical decomposition is related to initiation sensitivity of an energetic material because it is part of an initiation train sequence that produces catastrophic events [1]. Slowing the rate of the global thermochemical decomposition process, and the rate of energy release, can decrease the initiation sensitivity threshold of an energetic material, but it also can affect energetic material performance characteristics.

Performance. A graphic example is illustrated by the KDIE results seen in the high pressure combustion of identically synthesized HMX/HMX-d_8 samples and RDX/RDX-d_6 compounds [24,31]. Burn rate measurement of HMX and HMX-d_8 produced a KDIE equal to 1.37 at 500 psig as well as a KDIE of 1.60 at 1000 psig. These primary KDIE values suggest that the HMX combustion ultimately is regulated by the rate-controlling C-H bond rupture in the rapid solid state HMX thermochemical decomposition process which is part of the entire multi-faceted combustion phenomenon [24]. This rate-controlling mechanistic feature reduces combustion performance characteristics by significantly lowering the HMX burn rate. An analogous burn rate investigation of RDX and RDX-d_6 also provided a primary KDIE response where the burn rate of RDX was significantly faster than its RDX-d_6 analogue [31].

Concerning the effect of thermochemical decomposition on explosive performance, a laser induced rapid decomposition experiment with solid state RDX further provides some relevant information. This experiment shows that the more energy placed into the RDX sample by a laser pulse of specific time duration, the lower is the molecular weight of the product gases produced

[49]. Lower molecular weight gases result from a more complete thermochemical decomposition process occurring within a specific segment of time. Within this laser pulse time period, a higher amount of energy placed into the RDX sample produces more rapid kinetically governed chemical reaction sequences and a resultant faster rate-controlling step which drives the thermochemical decomposition process to a greater degree of completion. A more complete thermochemical decomposition generates a higher rate of energy release where more energy is available to drive the detonation wave front during an initiation train sequence.

This observed dependence of energetic material high energy performance on the energy release or generation rate of the thermochemical decomposition, like that exhibited in high pressure combustion and detonation, is further supported by a theoretical investigation conducted on solid phase nitromethane [13]. Calculations show that an increase in the bond dissociation energy by 3.45 kcal/mol (14.4 kJ/mol) behind the detonation wave front would decrease by 30 kcal/mol (125.5 kJ/mol) the energy of the chemical species which drive the detonation wave front. Thus, with the rate of energy generation reduced by an increase in bond dissociation energy, the velocity of the wave front is decreased which ultimately is reflected in a lower detonation velocity. Slowing the kinetics of the bond dissociation in the rate-controlling step, during a thermochemical decomposition process, decreases the amount and rate of energy being generated to drive the detonation wave front. This results in a decrease in wave front velocity as it moves through the energetic material during its finite initiation time period and gives a lower measured detonation velocity. In condensed phase energetic material initiation, the energy to drive the detonation wave front, ultimately is derived from the thermochemical decomposition process and is controlled to a significant extent by the rate at which decomposition proceeds. Thus, the kinetically governed rate-controlling step in the thermochemical decomposition process impacts the resultant detonation velocity.

Because gas phase decomposition reactions proceed more rapidly than those in the condensed phase, the energy available to drive the detonation wave front ultimately depends upon the kinetically governed reaction rates during the condensed phase thermochemical decomposition process. A decrease in the rate of the global thermochemical decomposition process, by a rate-controlling deuterium atom substitution, ultimately reduces the measured detonation velocity of an energetic material. The KDIE energy difference between a rate-controlling C-H and C-D bond rupture (dissociation) during the condensed phase thermochemical decomposition process

is 2.3 kcal/mol (9.6 kJ/mol). As a general linear approximation for the reported theoretical calculations [13], the bond dissociation energy increase of 2.3 kcal/mol (9.6 kJ/mol) in the rate-controlling mechanistic step of the condensed phase thermochemical decomposition would decrease the energy driving the detonation wave front by 20 kcal/mol (83.7 kJ/mol) [1] and result in a reduced detonation velocity. This velocity decrease in the detonation wave front, while effecting some degree of desensitization, also decreases energetic material performance, as experimentally verified, by the lower detonation velocity reported [32]. The rate-controlling feature inherent with the TNT thermochemical decomposition process (C-H bond rupture) [30] effects the detonation performance of the TNT energetic material [33, 48].

Returning to the shock initiation studies conducted with TNT and TNT-α-d_3 [33], KDIE evidence is seen where the molecular level rapid thermochemical decomposition component of the detonation phenomenon affects the detonation performance. The slower rate-controlling C-D bond rupture in TNT-α-d_3 reduces the rate at which the thermochemical decomposition process proceeds, which in turn, produces a statistically significant lower detonation velocity (6.145 mm/μsec) for TNT-α-d_3 compared to normal TNT (6.431 mm/μsec - the average of two control runs). This resultant detonation velocity gives a TNT /TNT-α-d_3 ratio equal to 1.05 which is similar to the analogous inversely related TNT-α-d_3/TNT ratio of 1.11 found for the flyer plate initiation velocity. These very similar ratios suggest that kinetic control, reflected by the KDIE response of TNT, plays a major role in its resultant detonation performance [50]. Thus, not only is initiation sensitivity affected by the rate at which rapid thermochemical decomposition proceeds, but detonation performance also shows a dependence on the kinetically governed rate-controlling step (C-H bond rupture) which regulates the rate at which the rapid thermochemical decomposition process proceeds.

Summary

The initiation of an energetic material to a high energy catastrophic event is a complex sequential chain of interacting mechanistic processes. These processes begin at the macroscopic or bulk compositional level, and sequentially move into the microscopic crystalline level, then into the sub-microscopic molecular and atomic levels, until final gaseous products and a concomitant energy release are observed at the bulk level (Figure 1). The mechanistic processes, which comprise this sequential initiation train, must occur within a finite time period at a rate

which produces enough energy to reach the required detonation threshold. Not achieving this rate dependent initiation threshold results in desensitization or lower performance characteristics for a given energetic material. Thus, energetic material initiation sensitivity and performance are defined in part by mechanistic rates.

The mechanistic processes in the initiation train sequence have three functions. The first function is to form the physical environment (defects) and use the existing defects at the bulk compositional level where subsequent mechanistic functions can proceed. The second function involves the crystalline level where mechanistic processes generate, transfer, and concentrate heat energy and effect non-thermal radical species formation in newly formed defects to introduce hot spots. The third function occurs at the molecular and atomic levels beginning in the newly formed hot spots. Here, kinetically controlled condensed phase, and later gas phase, thermochemical decomposition processes release the energy and form the species at a sufficient rate needed to achieve initiation and to sustain the catastrophic event.

Elucidation of these mechanistic processes involved with energetic material initiation is complex and difficult. Use of the kinetic deuterium isotope effect (KDIE) approach in ambient pressure thermochemical decomposition processes permits one to isolate and determine the rate-controlling bond rupture which constitutes the rate-limiting mechanistic feature of this process at the molecular level. Furthermore, for given energetic material, KDIE experiments conducted with deflagration, combustion, and explosion phenomena, reflect that, the same rate-controlling mechanistic feature in the ambient pressure thermochemical decomposition process, also appears as a significant rate controlling feature in these higher order phenomena. The KDIE approach establishes a relationship between the thermochemical decomposition process and both energetic material initiation sensitivity and performance characteristics.

Both theoretical and experimental KDIE-based investigations with energetic material combustion, thermal explosion, and detonation define the relationship of molecular level energetic material thermochemical decomposition with initiation sensitivity and performance. A decrease in the rate of energy, released or generated by the thermochemical decomposition process, will decrease initiation sensitivity and performance. When deuterium labeling of an energetic compound introduces a kinetically governed rate-controlling chemical bond rupture, and this bond rupture regulates a slower energy release rate in the resultant thermochemical decomposition process, lower initiation sensitivity, slower burn rates, and reduced detonation

velocity result. Thus, the rate-controlling step of molecular level thermochemical decomposition exerts a significant impact on energetic material sensitivity and performance behavior.

References

[1] Shackelford, S. A., A General Concept Concerning Energetic Material Sensitivity and Initiation, *J. de Physique. IV, Colloque C4*, Suppl. to *J. de Phys. III,* **1995**, *5*, C4-485 to C4-499. Portions of ref. [1] previously were presented at the following conferences: (a) *Workshop on Macroscopic and Microscopic Approaches to Detonation,* San Malo, France, 2-7 Oct **1994**, ; (b) *Eighteenth International Pyrotechnics Seminar*, Breckenridge, CO (USA) 13-18 Jul **1992**; (c) *Workshop on Desensitization of Explosives and Propellants*, Rijswijk, The Netherlands, 11-13 Nov **1991**;

[2] Shackelford, S. A., Mechanistic Investigations of Condensed Phase Energetic Material Decomposition Processes using the Kinetic Deuterium Isotope Effect, in: S. N. Bulusu (Ed.), *Chemistry and Physics of Energetic Materials*: Proceedings of the NATO Advanced Study Institute, Vol. 309, Kluwer Academic Publishers, Dordrecht, NL, **1990**, pp. 413-432 (Chapter 18), and references therein.

[3] Shackelford, S. A., Mechanistic Relationships of the Decomposition Process to Combustion and Explosion Events from Kinetic Deuterium Isotope Effect Investigations, *Ibid*., pp 433-456 (Chapter 19), and references therein.

[4] Field, J. E., Hot Spot Ignition Mechanisms for Explosives, *Acc. Chem. Res.*, **1992**, *25*, 489-496.

[5] Bowden, F. P., Yoffe, A. D. *Initiation and Growth of Explosives in Liquids and Solids*, Cambridge University Press: Cambridge, **1958**, reprinted 1989, in ref. [2].

[6] Coffey, C. S., Sharma, S., Lattice Softening and Failure in Severely Deformed Molecular Crystals, *J. Appl. Phys*. **2001**, *89*, 4797-4802.

[7] Sharma, S., Hoover, S. M., Coffey, C. S., Tompa, A. S., Sandusky, H. W., Armstrong, R. W., Elban, W. L., Structure of Crystal Defects in Damaged RDX as Revealed by an AFM, in: Schmidt, Dandekar, & Forbes (Eds.), *Shock Waves in Condensed Phase Matter-1997*; The American Institute of Physics, **1998**, pp. 563-566.

[8] Armstrong, R. W., Dislocation Mechanisms for Shock-Induced Hot Spots, *J. de Physique IV, Colloque C4*, Suppl. to *J. de Phys. III*, **1995**, *5*, C4-89 to C4-102, and references therein.

[9] (a) Zeman, S., Miloslav, K., New Aspects of Impact Reactivity of Polynitro Compounds, Part III. Impact Sensitivity as a Function of the Intermolecular Interactions, *Propellants, Explos., Pyrotech.*, **2003**, *28*, 301-307, and references therein.

[10] Lecume, S., Boutry, C., Spyckerelle, C., Structure of Nitramines Crystal Defects Relation

with Shock Sensitivity, 35th International Conference of ICT, Karlsruhe, FRG, 29 Jun-2 Jul **2004**, pp. 2-1 to 2-14. For completeness, it is noted that ref. [10] discusses the existence of internal (crystal interior) and external (crystal surface and edges) defects in an energetic material crystal lattice and reveals that external defects more readily affect initiation sensitivity.

[11] Walker, F. E., A New Kinetics and the Simplicity of Detonation, *J. de Physique. IV, Colloque C4*, Suppl. to *J. de Phys. III*, **1995**, *5*, C4-309 to C4-333.

[12] Dick J. J., Orientation-Dependent Explosion Sensitivity of Solid Nitromethane, *J. Phys. Chem*., **1993**, *97*, 6193-6196.

[13] Odiot, S., Fundamental Physics and Chemistry Behind Molecular Crystal Detonations at the Microscopic Level, in: S. N. Bulusu (Ed.), *Chemistry and Physics of Energetic Materials*; Proceedings of the NATO Advanced Study Institute, Vol. 309, Kluwer Academic Publishers: Dordrecht, NL, **1990**, pp. 79-130 (Chapter 5).

[14] (a) Dick, J. J., Mulford, R. N., Spencer, W. J., Pettit, D. R., Garcia, E.; Shaw, D. C., Shock Response of Pentaerythritol Tetranitrate Single Crystals, *J. Appl. Phys*., **1991**, *70*, 3572-3587; and, (b) Dick, J. J., Orientation Dependence of the Shock Initiation Sensitivity of PETN: A Steric Hindrance Model, Workshop on Desensitization of Explosives and Propellants, Rijswijk, The Netherlands, 11-13 Nov **1991**.

[15] Piermarini, G. J., Block, S., Miller, P. J., Effects of Pressure on the Thermal Decomposition Kinetics and Chemical Reactivity of Nitromethane, *J. Phys. Chem*., **1989**, *93*, 457-462.

[16] Samirant, M., Detonation des Monocristaux. Analyse Experimentale Limites, *J. de Physique (Colloque C4)*, **1987**, *48*, 85-98.

[17] Zeman, S., New Aspects of the Impact Reactivity of Nitramines, *Propellants, Explos., Pyrotech.*, **2000**, *25*, 66-74.

[18] Dremin, A. N., Klimenko, V. Yu., Davidova, O. N., Zoludeva, T. A., *Proc. of the Ninth Symposium (International) on Detonation*, 28 Aug – 1 Sep **1989**, Portland, OR (USA), in reference [19].

[19] Sharma, J., Chemistry of Energetic Materials Under Shock Caused Via Electronic Excitations, in: S. C. Schmidt, R. D. Dick, J. W. Forbes, D. G. Tasker (Eds.), *Shock Compression of Condensed Phase Matter-1991*;.; Elsevier Science Publishers, **1998**, pp. 639-645.

[20] Zeman, S., New Aspects of Impact Reactivity of Polynitro Compounds, Part IV. Allocation of Polynitro Compounds on the Basis of their Impact Sensitivities, *Propellants, Explos., Pyrotech*., **2003**, *28*, 308-313.

[21] Brill, T. B., Patil, D. G., Duterque, J., Lengelle, G., Thermal Decomposition of Energetic

Materials 63. Surface Reaction Zone Chemistry of Simulated Burning 1,3,5,5-Tetranitrohexahydropyrimidine (DNNC or TNDA) Compared to RDX, *Combust. Flame*, **1993**, *95*, 183-190.

[22] Hendrickson, S. A., Shackelford, S. A., Solid State Thermochemical Decomposition of Neat 1,3,5,5-Tetranitrohexahydropyrimidine (DNNC) and its DNNC-d_6 Perdeuterio-Labeled Analogue, *Thermochim. Acta,* **2006**, *440*, 146-155.

[23] Shackelford, S. A., Menapace, J. A., Golden, J. F., Hendrickson, S. A., Solid State Versus Liquid State Thermochemical Decomposition Comparison of 1,3,5,5-Tetranitrohexahydro-pyrimidine (DNNC) and DNNC-d_6: Role of Chemical Structure Revisited, 35th International Conference of ICT, Karlsruhe, FRG, June 29 to July 2, **2004**, pp. 43-1 to 43-15.

[24] Shackelford, S. A., Goshgarian, B. B., Chapman, R. D., Askins, R. E., Flanigan, D. A., Rogers, R. N., Deuterium Isotope Effects During HMX Combustion: Chemical Kinetic Burn Rate Control Mechanism Verified, *Propellants, Explos., Pyrotech*., **1989**, *14*, 93-102.

[25] Lee, J., Combustion and Turbulence I., NATO Advanced Study Institute on Chemical Reaction Dynamics, Iraklion (Crete), Greece, 25 Aug – 7 Sep 1985.

[26] Oran, E. S., Kailasanath, K., Guirguis, R. H., The Structure of Detonation Waves, *J. de Physique (Colloque C4)*, **1987**, *48*, 105-117.

[27] Dupre G., Cinetique Chimique et Detonation, *J. de Physique (Colloque C4)*, **1987**, *48*, 397-403.

[28] McGuire, R. R., Ornellas, D. I., Askt, I. B., Detonation Chemistry: Diffusion Control in Non-Ideal Explosives, *Propellants and Explos*., **1979**, *4*, 23-26.

[29] Shackelford, S. A., Coolidge, M. B., Goshgarian, B. B., Loving, B. B., Rogers, R. N., Janney, J. L., Ebinger, M. H., Deuterium Isotope Effects in Condensed-Phase Thermochemical Decomposition Reactions of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, *J. Phys. Chem.*, **1985**, *89*, 3118-3126, and references therein.

[30] Shackelford, S. A., Beckmann, J. W., Wilkes, J. S., Deuterium Isotope Effects in the Thermochemical Decomposition of Liquid 2,4,6-Trinitrotolulene: Application to Mechanistic Studies Using Isothermal Differential Scanning Calorimetry Analysis, *J. Org. Chem*., **1977**, *42*, 4201-4206.

[31] Shackelford, S. A., Rodgers, S. L., Askins, R. E., Deuterium Isotope Effects During RDX Combustion: Mechanistic Burn Rate-Controlling Step Determination, *Propellants, Explos., Pyrotech*., **1991**, *16*, 279-286.

[32] Rodgers, R. N., Janney, J. L., Ebinger, M. H., Kinetic Isotope Effects in Thermal Explosions, *Thermochim. Acta*, **1982**, *59*, 287-298.

[33] Bulusu, S., Autera, J. R., Initiation Mechanism of TNT: Deuterium Isotope Effect as an Experimental Probe, *J. Energetic Mater*., **1983**, *1*, 133-140.

[34] Bulusu, S., Weinstein, D. I., Autera, J. R., Velicky, R. W., Deuterium Kinetic Isotope Effect in the Thermal Decomposition of 1,3,5-Trinitro-1,3,5-triazacyclohexane and 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane: Its Use as an Experimental Probe for Their Shock-Induced Chemistry, *J. Phys. Chem*., **1986**, *90*, 4121-4126.

[35] Brill, T. B., James, K. J., Thermal Decomposition of Energetic Materials. 62. Reconciliation of the Kinetics and Mechanisms of TNT on the Time Scale from Microseconds to Hours, *J. Phys. Chem*., **1993**, *97*, 8759-8763.

[36] Makismov, Y. Y., Sopranovich, V. F., Ployakova, N. V., *Tr. Inst.-Mosk. Khim.-Tekhnol. Inst. im. D. I. Mendeleeva*, **1974**, *83*, 51, in reference [35].

[37] Robertson, A. J. B., The Decomposition, Boiling and Explosion of Trinitrotoluene at High Temperatures, *Trans. Faraday Soc*., **1948**, *48*, 977-983.

[38] Janney, J. L., Rogers, R. N., Experimental Thermochemistry Observations of Condensed-Phase Reactions, *Proceed. 11th North American Thermal Analytical Society Conference*, Vol. II, Oct **1982**, pp 643-649.

[39] Rodgers, S. L., Coolidge, M. B., Lauderdale, W. J., Shackelford, S. A., Comparative Mechanistic Thermochemical Decomposition Analyses of Liquid Hexahydro-1,3,5-Trinitro-1,3,5-triazine (RDX) Using the Kinetic Deuterium Isotope Effect Approach, *Thermochim. Acta*, **1991**, *177*, 151-168.

[40] (a) Behrens, R., Jr., Bulusu, S., Thermal Decomposition of Energetic Materials. 2. Deuterium Isotope Effects and Isotopic Scrambling in Condensed-Phase Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, *J. Phys. Chem*. **1991**, *95*, 5838-5845; and, (b) Behrens, R., Jr., Bulusu, S., Thermal Decomposition of Energetic Materials: Temporal Behaviors of the Rates of Formation of the Gaseous Pyrolysis Products from Condensed-Phase Decomposition of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, *J. Phys. Chem*., **1990**, *94*, 6706-6718.

[41] (a) Behrens, R., Jr., Bulusu, S., Thermal Decomposition of Energetic Materials. 4. Deuterium Isotope Effects and Isotopic Scrambling (H/D, $^{13}C/^{18}O$, $^{14}N/^{15}N$) in Condensed-Phase Decomposition of 1,3,5-Trinitrohexahydro-s-triazine, *J. Phys. Chem*., **1992**, *96*, 8891-8897; and, (b) Behrens, R., Jr., Bulusu, S., Thermal Decomposition of Energetic Materials. 3. Temporal Behaviors of the Rates of Formation of the Gaseous Pyrolysis Products from Condensed-Phase Decomposition of 1,3,5-Trinitrohexahydro-s-triazine, *J. Phys. Chem*., **1992**, *96*, 8877-8891.

[42] Sharma, J., Forbes, J. W., Coffey, C. S., Liddiard, T. P., The Physical and Chemical Nature of Sensitization Centers Left from Hot Spots Caused in Triaminotrinitrobenzene by Shock or

Impact, *J. Phys. Chem*., **1987**, *91*, 5139-5144.

[43] (a) Sharma, J., Hoffsommer, J. C., Glover, D. J., Coffey, C. S., Forbes, J. W., Liddiard, T. P., Elban, W. L., Santiago, F., Sub-Ignition Reactions at Molecular Levels in Explosives Subjected to Impact and Underwater Shock, *Proceedings: Symposium (International) on Detonation*, 8th, U.S. Government Printing Office, Washington, D.C., MP 86-194, **1987**, pp 725-733; and, (b) Hoffsommer, J. C., Glover, D. J., Elban, W. L., Quantitative Evidence for Nitroso Compound Formation in Drop-Weight Impacted RDX Crystals, *J. Energetic Mater*., **1985**, *3*, 149-167.

[44] Sharma, J., Forbes, J. W., Coffey, C. S., Liddiard, J. P., The Nature of Reaction Sites and Sensitization Centers in TATB and TNT, in: S. C. Schmidt, N. C. Holmes (Eds.), *Shock Waves in Condensed Phase Matter*, Elsevier Science Publishers, Amsterdam, **1987**, pp 565-568.

[45] Sharma, J., Hoffsommer, D. J., Glover, D. J., Coffey, C. S., Santiago, F., Stolovy, A., Yasuda, S., Comparative Study of Molecular Fragmentation in Sub-Initiated TATB Caused by Impact, UV, Heat, and Electron Beams, in: J. R. Asay, R. A. Graham, G. K. Straub (Eds.) *Shock Waves in Condensed Matter,* Elsevier Science Publishers, Amsterdam, **1983**, pp 543-546.

[46] Rogers, R. N., Combined Pyrolysis and Thin Layer Chromatography, *Anal. Chem*., **1967**, *39*, 730-733.

[47] Dacons, J. C.; Adolph, H. G.; Kamlet, M. J., Some Novel Observations Concerning the Thermal Decomposition of 2,4,6-Trinitrotoluene, *J. Phys. Chem*., **1970**, *74*, 3035-3040.

[48] Varga, R., Zeman, S., Decomposition of Some Polynitro Arenes Initiated by Heat and Shock. Part I. 2,4,6-Trinitrotoluene, *J. Hazard. Mater*., **2006**, 132, 165-170.

[49] Pfeil, A., Eisenreich, N., Krause, H., Analysis of Intermediate and Final Products of an Explosive Reaction, *J. de Physique (Colloque C4)*, **1987**, *48*, 209-221.

[50] A colleague pointed out that the momentum transfer of detonation products, given a fixed amount of energy, is less for heavier deuterated species (momentum control); and therefore, this momentum control also might explain the reduced detonation velocities observed between a given energetic material and its deuterated analogue. While this momentum effect might have some contribution to a reduced detonation velocity when an energetic material is deuterium labeled, when a KDIE operates (kinetic control), there is a decreased energy release rate, and a resultant total energy available to drive the initiating shock wave; therefore, a fixed amount of energy (same energy for both) cannot be a parametric condition when comparing the normal and deuterium labeled energetic material. Secondly, not all detonation products would contain deuterium atoms (*i.e.* CO, CO_2, N_2, etc.). Thirdly, the difference in flyer plate shock velocity to initiate TNT-α-d_3/TNT, where product species momentum should not be a consideration, gives a 1.11 ratio.[33] The resultant detonation velocity in mm/μsec, containing the product species, gives a very similar inversely related

TNT/TNT-α-d_3 ratio (6.431 /6.145 = 1.05).[33] These similar values likely suggest that kinetic control is the major contributor to the reduced detonation velocity found.

Acknowledgements. SAS especially thanks Prof. Svatopluk Zeman, NTREM Seminar chairman, for his gracious invitation to participate and speak at this annual scientific gathering. The author also wishes to thank the following individuals: Dr. John L. Belletire and Dr. Jeffery D. Mills, for critical comments and detailed review of this manuscript, Mr. Dean Richards for welcome computer graphics assistance, Mr. Wayne Kalliomaa, and Dr. Robert Corley for necessary manuscript processing support, and Dr. Steven A. Svejda for key managerial and financial support to attend the 10th NTREM Seminar. An invitation from Dr. Allen J. Tulis to give a paper at the 18th International Pyrotechnics Seminar resulted in the author first conceiving possible thermochemical decomposition KDIE data relationships to the total energetic material initiation sensitivity issue. Gratefully acknowledged also is the long-term support and encouragement Dr. R. H. Woodward Waesche has afforded SAS regarding mechanistic energetic material investigations based upon use of the KDIE approach.

Distribution A. Approved for public release; distribution unlimited.

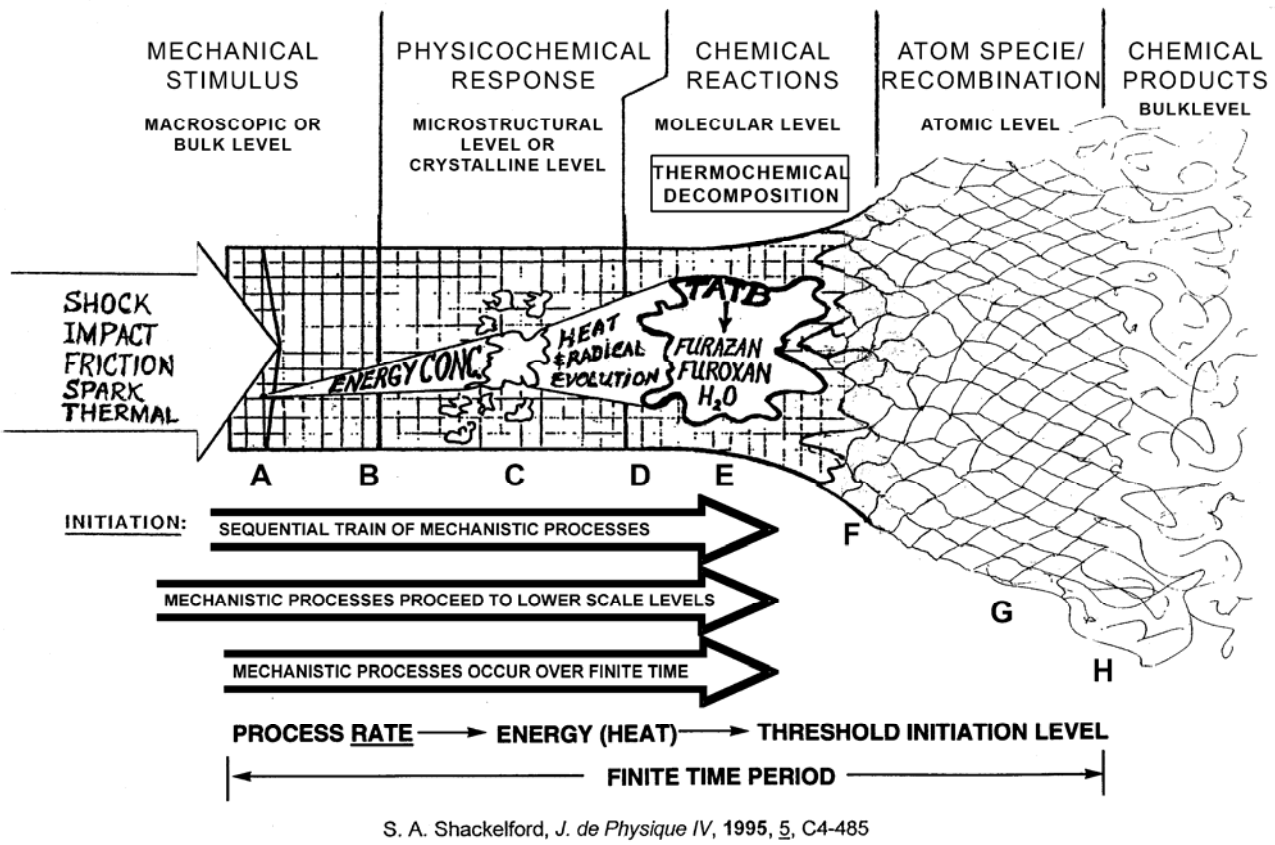


Figure 1. A General Concept Concerning Energetic Material Sensitivity and Initiation [1].

Distribution A. Approved for public release; distribution unlimited.

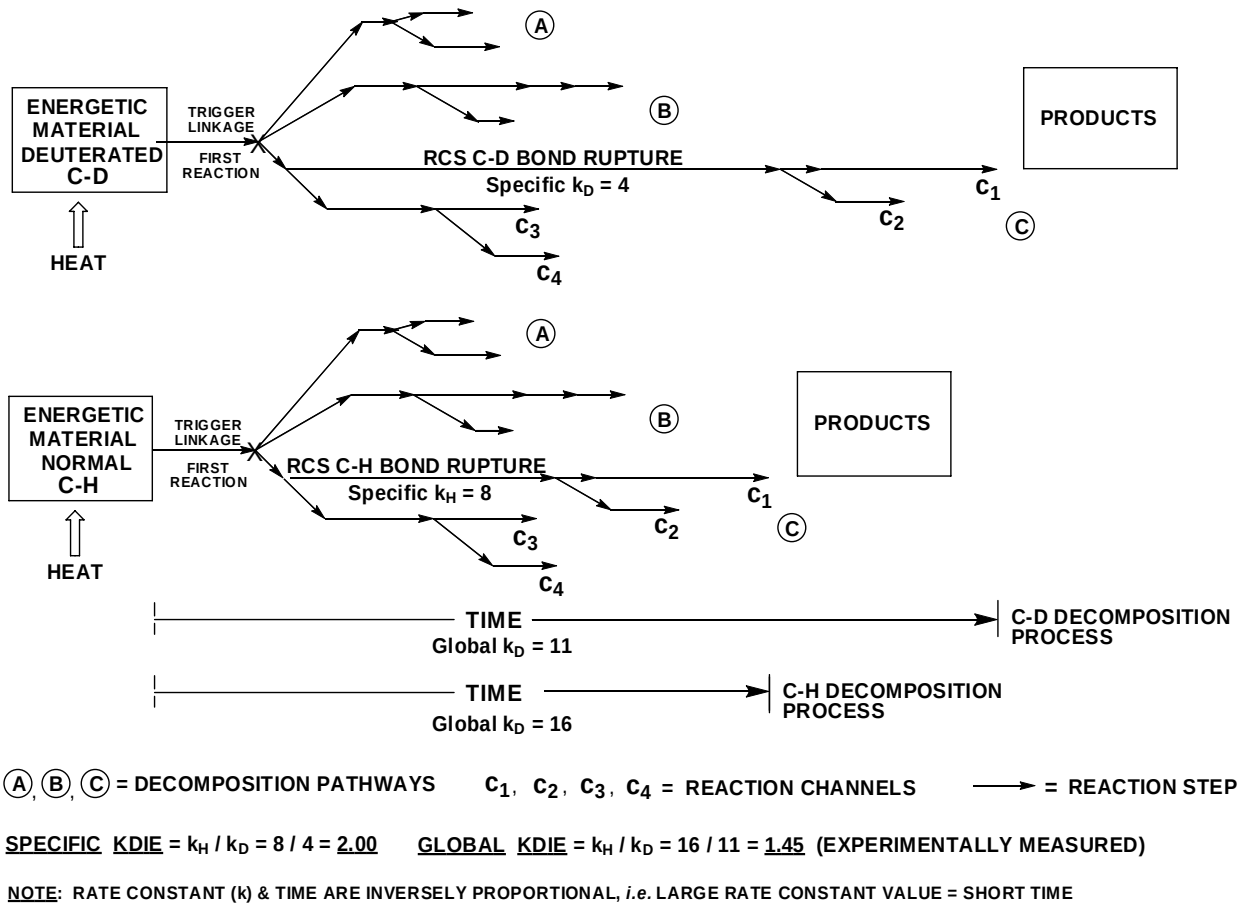


Figure 2. Schematic of Complex Thermochemical Decomposition Process with Rate-Controlling Step (RCS) and Resultant Experimentally Measured Global KDIE.

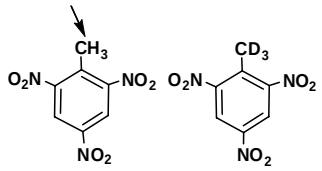
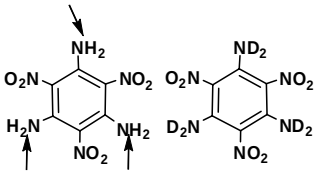
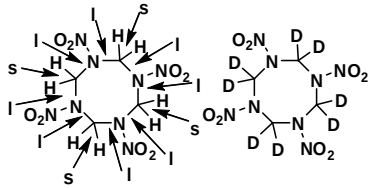
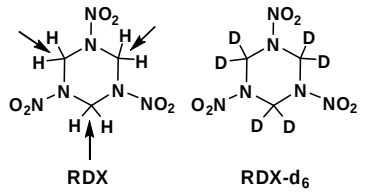
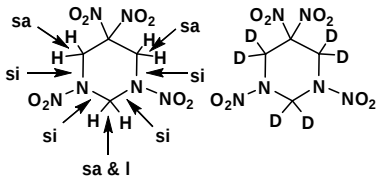
ENERGETIC MATERIAL	CONDENSED PHASE	DECOMPOSITION PORTION	KDIE TYPE	RCS BOND RUPTURE SITE →	REFERENCE CITATIONS
 TNT TNT-alpha-d_3	LIQUID	FIRST HALF OF PROCESS	PRIMARY	C-H	[30]
 TATB TATB-d_6	SOLID	ENTIRE PROCESS	PRIMARY	N-H	[32]
 HMX HMX-d_8	SOLID	INDUCTION PERIOD	PRIMARY	C-H @ s positions s = solid phase	[29],[34]
	MIXED MELT	ACCELERATORY PERIOD	INVERSE	CRYSTAL LATTICE FORCES	[29]
	LIQUID	DECAY PERIOD	SECONDARY	RING C-N @ l positions l = liquid phase	[29]
 RDX RDX-d_6	SOLID	ENTIRE PROCESS	PRIMARY	C-H	[34]
	LIQUID	ENTIRE PROCESS	PRIMARY	C-H	[34],[39]
 DNNC DNNC-d_6	SOLID	INDUCTION PERIOD	SECONDARY	RING C-N @ si positions si = solid state induction period	[22]
		ACCELERATORY PERIOD	PRIMARY	C-H @ sa positions sa = solid state acceleratory period	[22]
	LIQUID	ENTIRE PROCESS	PRIMARY	C-H @ l position only l = liquid state entire process	[23]

Figure 3. KDIE Based Thermochemical Decomposition Rate-Controlling Step **(RCS)** of Various Energetic Materials Determined at Ambient Pressure.

Distribution A. Approved for public release; distribution unlimited.

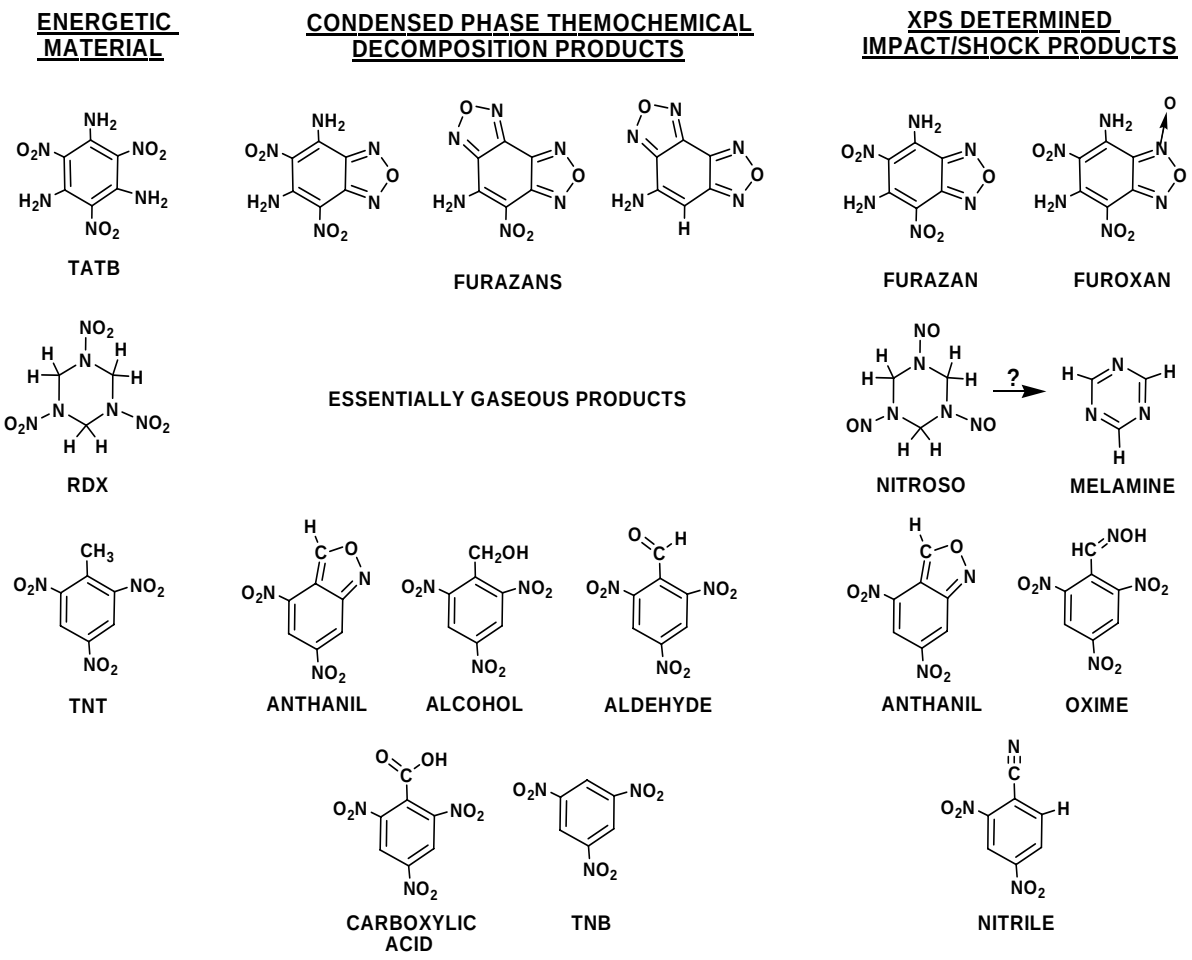


Figure 4. Condensed phase product comparison: Thermochemical Decomposition, TATB [45], TNT [46,47]; Impact/Shock, TATB [42], RDX [43], TNT [44,48].

Distribution A. Approved for public release; distribution unlimited.